# Atmosphere Issues in Detection of Explosives and Organic Residues

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## ABSTRACT

This study makes a comparison of LIBS emission from molecular species in plasmas produced from organic residues on a non-metallic substrate by both a 5 ns Nd:YAG laser (1064 nm) and a 40 fs Ti:Sapphire laser (800 nm) in air and argon atmospheres. The organic samples analyzed had varying amounts of carbon, nitrogen, hydrogen, and oxygen in their molecular structure. The characterization was based on the atomic carbon, hydrogen, nitrogen, and oxygen lines as well as the diatomic species CN ($B^2\Sigma^+$ - $X^2\Sigma^+$) and the $C_2$ ($d^3\Pi_g$ - $a^3\Pi_u$). Principal Component Analysis (PCA) was used to identify similarities of the organic analyte via the emission spectra. The corresponding Receiver Operating Characteristics (ROC) curves show the limitations of the PCA model for the nanosecond regime in air.

**Keywords:** Organic residues, explosive residues, atomic spectroscopy, molecular spectroscopy, laser induced breakdown spectroscopy, principal component analysis, receiver operator characteristics curves

## 1.   INTRODUCTION

The ability to discriminate energetic materials from other organic samples has been a pressing issue in the field of detection.[1,2,3] As the unlawful use of energetic materials continues to evolve, so too must the detection and regulation of these dangerous chemicals. In order to detect energetic materials in all forms, they must be studied and characterized. It is important to understand the influence of the surrounding atmosphere on the LIBS analysis of organic materials, which are largely comprised of carbon, nitrogen, hydrogen, and oxygen. Previous studies have shown that atmospheric nitrogen and oxygen can be ionized together with sample constituents, and as a consequence skew the interpretation of the resulting spectra. This becomes extremely important when trying to detect explosives, due to the fact that most energetic compounds contain higher mole fractions of oxygen and nitrogen compared to the carbon and hydrogen in non-energetic organic materials.

The main objective of this study is to answer the question of whether or not it is possible to detect and discriminate energetic materials in a single laser shot in air atmosphere. As such this study focuses on characterizing the spectroscopic signatures of organic residues in various laser regimes, and understanding how the atmosphere may play a role in the skewing of the detection and discrimination. All of this leads to answering the questions of whether

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or not organic residues can be detected, and if explosives can successfully be discriminated from various other organics.

## 2. BACKGROUND

### 2.1 Laser-Induced Breakdown Spectroscopy

Laser-Induced Breakdown Spectroscopy (LIBS) is the selected spectroscopic technique for this study due to the power of this technique to facilitate the gathering of information on both atomic and molecular emission in a single laser shot. An example of a LIBS spectrum is shown in Figure 1 with selected atomic and molecular emissions identified.
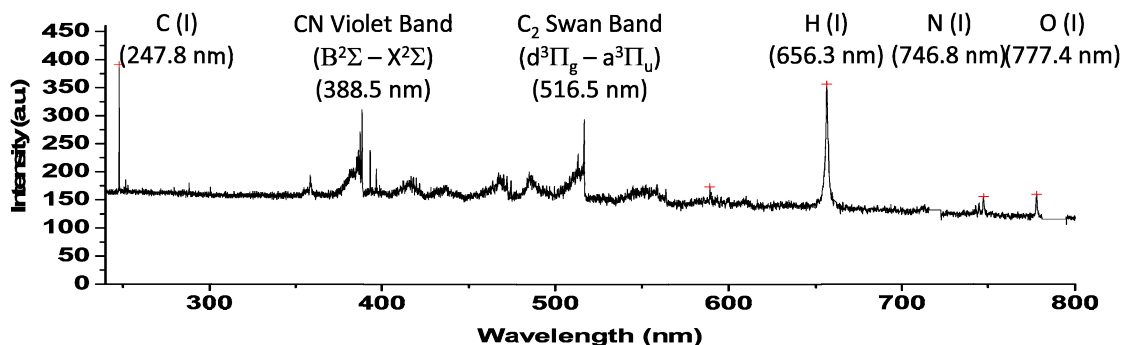


Fig 1. LIBS Spectrum of Graphite in air environment with a nanosecond laser.

While information on both the atomic and molecular emission is collected one must be careful when identifying and assigning the emitting species. The LIBS plasma is a complex system that consists of interactions not only of the laser with the sample, but also the laser with the plasma and the plasma with the atmosphere. This is a particularly important issue when dealing with organic samples, due to the fact that many of the elements that are selected as discriminators are also commonly found in air. As previous papers have shown, it is possible for the atmosphere to play a critical role in the plasma emission.[4,5] Upon examination of the spectrum shown in Figure 1 there is clear evidence of molecular CN emission, even though are no CN bonds in graphite. This leads one to attribute the CN emitter as a molecular recombination between the native carbon (atomic and/or molecular) and the atmospheric $N_2$. In order to correctly identify the source of the nitrogen, LIBS spectra were taken under a variety of atmospheres.

### 2.2 Constructing an Analytical Model using Principal Component Analysis (PCA)

Due to the large amount of cross-correlated information gathered from LIBS, an analytical technique that is capable of quickly and efficiently sifting through the large amount of data is required. Principal component analysis (PCA) is selected as a multivariate analysis technique.[6,7] It can be summarized as a method of transforming the originally selected variables into a new set of uncorrelated variables called principal components (PCs), each of which is a linear combination of the original variables.[8] Each PC is optimized to account for the greatest possible fraction of variance in the original data.

Using five spectra for each sample from a test scenario, the intensity from the selected spectral line emission is averaged for each variable per respective sample. In order to determine if the variable peak is statistically

significant, the peak intensity has to be three times larger than the surrounding noise. If this condition is found to be false, a null value is placed in the variable's place holder and not the peak intensity. These data are then used to construct the data matrix, which is shown in Figure 2.
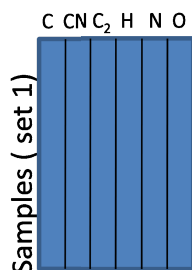


Fig 2. Construction of the Original Data Matrix

In order to construct the PCs, the covariance matrix of the data is first created. The covariance matrix is needed in order to determine the highest variance and the lowest covariance among the variables. The data matrix is then pre-multiplied by its transpose, the product of which is the covariance matrix (Fig 3).
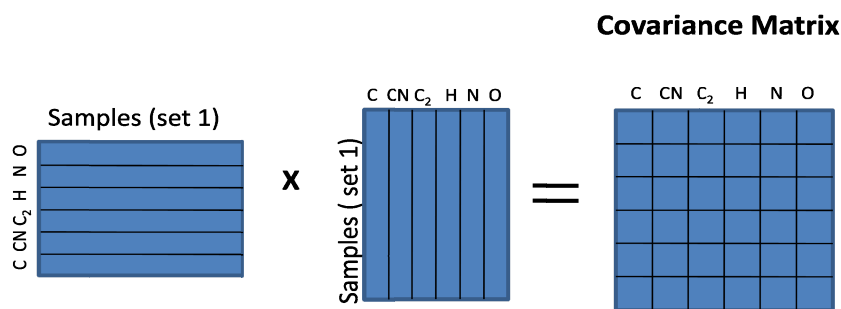


Fig 3. Construction of the Covariance Matrix

By performing an eigenanalysis (diagonalization) on the covariance matrix (Fig 4), we obtain eigenvectors and eigenvalues that form a new basis of ortho-normal vectors.
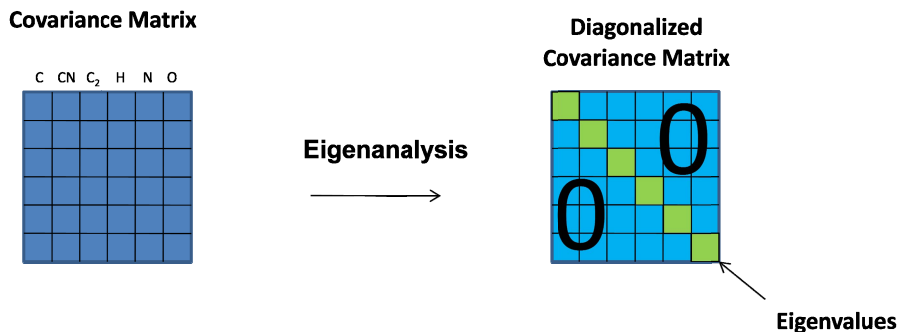


Fig 4. Diagonalization of the Covariance Matrix

The resulting eigenvectors of the eigenanalysis are known as the principal components (PC), and the eigenvalues are the variances of the PCs. The eigenvectors are made up of *Loadings* or the coefficients of the linear combination of the original variables.

The PCs with the variance contributing to 99% of the total variance are selected, in order to optimize the data and reduce the noise and redundancy in the data set. For example, in our case (Fig 5) the first three variances (eigenvalues) constitute over 99% of the variance for the data set. Therefore the last three variances would only add noise and redundancy back to the data.
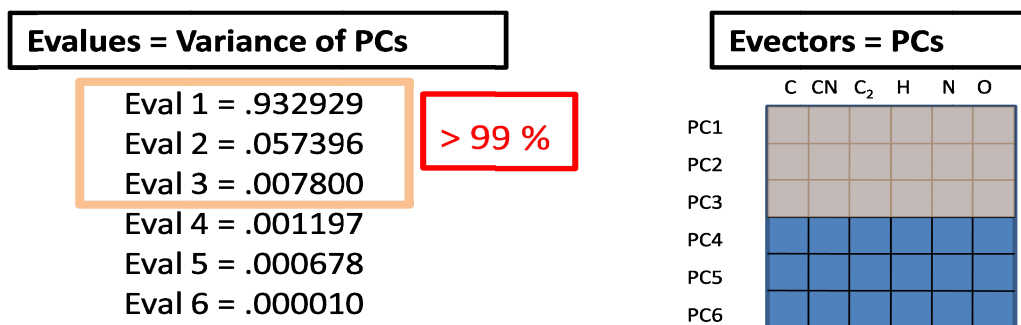


Fig 5. Results of the Eigenanalysis performed on the Covariance Matrix.

Projecting the original data matrix onto the subspace of the first three PCs yields the *Model Scores* (Fig 6), or the coordinates of the data matrix transformed into the new basis.
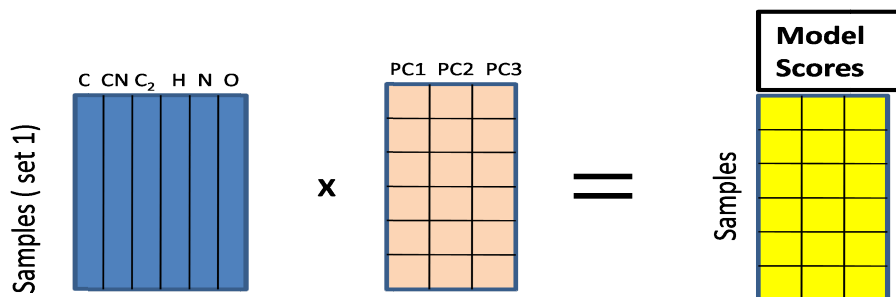


Fig 6. Construction of the model scores for the analytical model.

The model scores constitute the reference or the library against which tests of the same scenario are measured.

Test scores are derived from a second set of five single shot LIBS spectra from the same samples. The same procedure of generating the original data matrix is followed in order to produce the second data matrix. The second data matrix is then multiplied by the same PCs generated in the model construction, the product of which yields the *Test Scores* (Fig 7).
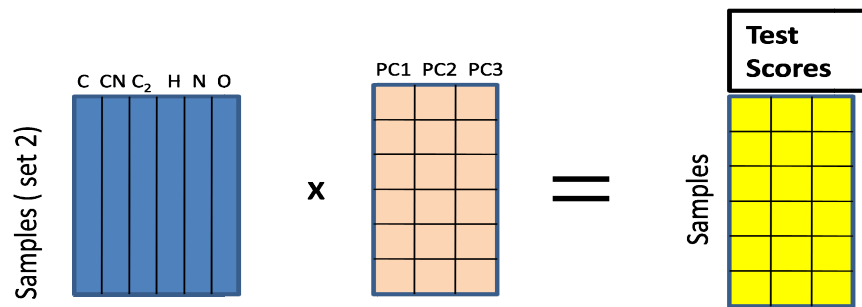
Fig 7. Construction of the test scores, which are compared to the model scores.

The test scores are then compared to the model scores, by calculating the Euclidean Distance between them.

Along the diagonal of the Euclidean Matrix (Fig 8) the distance in the ideal case would be zero, since the sample is compared to itself. However, due to uncontrollable factors such as the shot-to-shot stability of the laser, the distance may not be null. Distances in the off-diagonal however, should result in distances greater than those in the diagonal due to the fact that different samples are being compared.
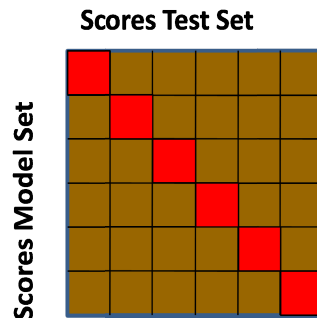


Fig 8. Resultant matrix in which the Euclidean distance is calculated between the model scores and the test scores.

## 2.3     Evaluating the Analytical Model with Receiver Operator Characteristic (ROC) Curves

Receiver Operator Characteristic (ROC) Curves were used to evaluate the analytical models that are constructed. Traditionally, the ROC curve is comprised of a plot of the *sensitivity* (the proportion of the correctly identified samples) versus the *1-specificity* (the proportion of incorrectly identified samples). The values constituting the sensitivity were known as the "true positives", while the values constituting the 1-specificity were known as the "false positives".
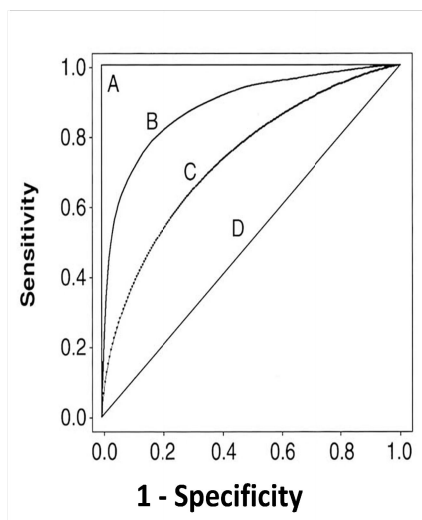
Fig 9. Examples of Receiver Operator Characteristic Curves.
(Courtesy of http://kjronline.org/abstract/journal_figure.asp?img=v5n1011fig2.jpg&no=354&desc=desc5)

Figure 9 shows examples of ROC curves. Curve A represents an ideal ROC curve (in this case perfect discrimination) in which the area under the curve is 1.0. This means that all of the true positive values are assigned before any false positive value based on a given figure of merit (the Euclidean distance in the case discussed here). Curve D on the other hand, represents the opposite extreme case, that of random discrimination. This means that there is equal probability of assigning either a true positive or a false positive. As such, the area under Curve D is 0.50. Curves B and C represent examples of real solutions, and since the Curve B has a greater area than that of Curve C, Curve B would be considered a better analytical technique than the technique used by Curve C. Thus, the higher the area under the curve, the higher the specificity and sensitivity of the analytical technique.

In this study, the Euclidean distance is used as a metric to generate the ROC curves, with the values along the diagonal of the resultant matrix (Fig. 8) were considered to be the true positives, while values in the off-diagonals were the false positives.

## 3.   EXPERIMENTAL SETUP

The experimental setup shown below is used in order to systematically characterize the spectroscopic signatures of the organic sample set.
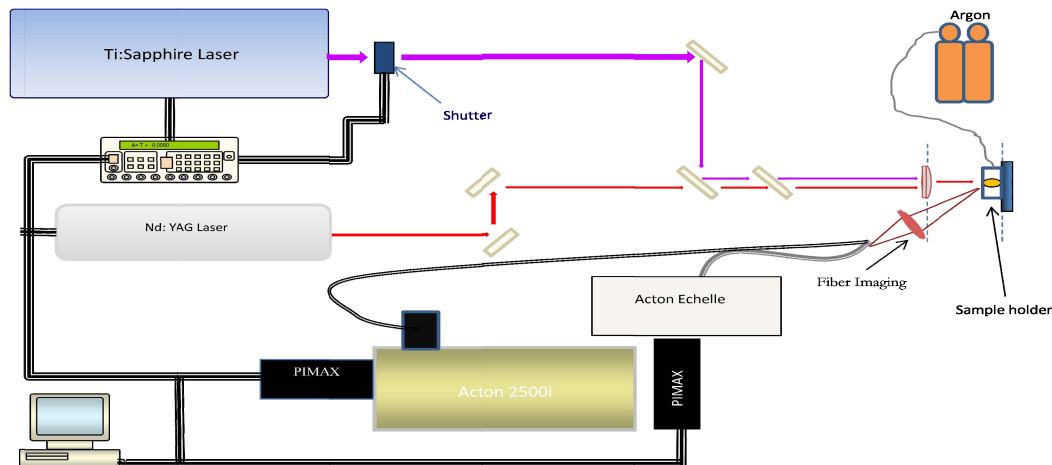
Fig 10. Picture of the experimental setup utilized for controlled conditions for single shot analysis.

## 3.1 Laser Sources

### 3.1.1 Femtosecond Laser

The femtosecond laser system used consists of a chirped pulse amplified (CPA) Ti:Sapphire laser. The oscillator (Tsunami- Spectra Physics) is pumped by a doubled continuous-wave $Nd:YVO_4$ crystal laser (Millennia Pro- Spectra Physics). The pulses are shaped through an acousto-optical programmable dispersion filter (Dazzler-Fastlite) in order to pre-compensate for the dispersion that occurs inside the amplifying chain. The amplifier is pumped by a Nd:YLF laser (Evolution- Spectra Physics), and seeded by the pulses which have been stretched. Before being compressed the amplified pulses are further amplified in a double-pass amplifier pumped by a Nd:YAG laser (Quanta-Ray – Spectra Physics) The system produces pulses of 2.4 mJ energy, in a beam diameter of approximately 6 mm FWHM and is focused using a 100 cm convex lens. The pulse width is approximately 40 fs and is centered at wavelength of 800 nm. Although the laser is run at repetition rate of 10 Hz, a mechanical shutter is used in order to allow single shot analysis.

### 3.1.2 Nanosecond Laser

The nanosecond LIBS experiments are performed using a Quantel Brilliant laser. This Nd:Yag laser is used at its fundamental wavelength of 1064 nm, and run at repetition rate of 10 Hz with a pulse width of approximately 5 ns. The beam diameter is approximately 6 mm and is focused using a 7.5 cm convex lens. A light valve is used to reduce the pulse energy to 12 mJ. In order to ensure that only a single shot is fired, the single shot mode is used to fire the pockel cell.

## 3.2 Sample Chamber

The sample chamber that is used allows for both an open air and an argon environment. In addition to these full environments, the sample chamber also allows for an argon jet of 20 psi backing pressure to flow in front of the sample.

## 3.3 Collection Optics and Spectrometers

The same light collection scheme is used throughout the entire experiment. The light from the plasma is collected by a collimating lens (74-UV- Newport) and focused onto a 500 μm fiber. The fiber is coupled to a 0.5 m Czerny-

Turner spectrometer (2500i – Acton) equipped with both a 150 l/mm grating as well as a 600 l/mm grating. The spectrometer is equipped with an iCCD camera (PI Max Gen II Princeton). Although the same collection optics were used throughout the experiments the collection timings for the recorded spectra are different. For the femtosecond spectra the detector gate width is 50 μsec and is delayed 40 ns after the laser, while the nanosecond spectra has a gate width of 10 μsec and is delayed 50 ns after the laser.

## 3.4    Organic Samples

A variety of organic samples was used throughout the experiment, and can be found in Table 1.

Table 1. List of organic samples and their respective solvent: ethanol (ETOH), acetonitrile (ACN), and water ($H_2O$). The explosives are denoted in italics.

| | |
|---|---|
| 4- nitrotoluene (p-NT) / (ACN) | *2,4,6- Trinitrotoluene (2,4,6-TNT)* / (ACN) |
| 1,2- Dinitrobenzene (1,2-DNB) / (ACN) | *Cyclo-1,3,5- trimethylene -2,4,6- trinitramine (RDX)* / (ACN) |
| 1,4- Dinitrobenzene (1,4-DNB) / (ACN) | 1,2,4,5- Benzenetetracarboxylic acid (BTCA) / (ETOH) |
| 1,3- Dinitrobenzene (1,3-DNB) / (ACN) | Benzoic Acid (BA) / (ETOH) |
| 2,3- Dinitrotoluene (2,3-DNT) / (ACN) | Benzophene (BP) / (ETOH) |
| 2,4- Dinitrotoluene (2,4-DNT) / (ACN) | Polyacrylic Acid (PAA) / ($H_2O$) |
| 3,4- Dinitrotoluene (3,4-DNT) / (ACN) | Pthalic Acid (PA) / (ETOH) |
| Tris (hydroxmethyl) aminomethane (Tham) / ($H_2O$) | Fluoranthene (Fluor) / (ETOH) |
| Theophylline (TP) / ($H_2O$) | 1- Cyanonaphthalene (CN) / (ETOH) |

The samples are all prepared in a similar fashion. The organic sample is first measured and mixed with the appropriate amount of solvent (acetonitrile, ethanol, and water.) in order to achieve a 1000 ppm solution. Using an Eppendorf pipette, 70 μL are deposited onto a 1 cm x 1 cm square silicon wafer substrate. Enough time is allowed to elapse in order to let the solvent evaporate thus leaving only an organic residue. In the case of the water solvent, the wafer is placed on a hot plate in order to evaporate the water. The organic residue concentration is on the order of 50 μg/cm$^2$, which results in a thickness of approximately 500 nm; however, the residues are not evenly distributed.

## 4.    RESULTS and DISCUSSION

Upon applying the PCA analytical model to the various laser regimes the following ROC plots were generated. The analytically built models were constructed using a Czerny-Turner spectrometer for detection. This leads to a significant increase in the variability of the spectra due to having to take six laser shots, in order to complete one spectrum (1 acquisition per spectral variable). Although the laser used was fairly stable there was still a shot-to-shot fluctuation of approximately 8%.
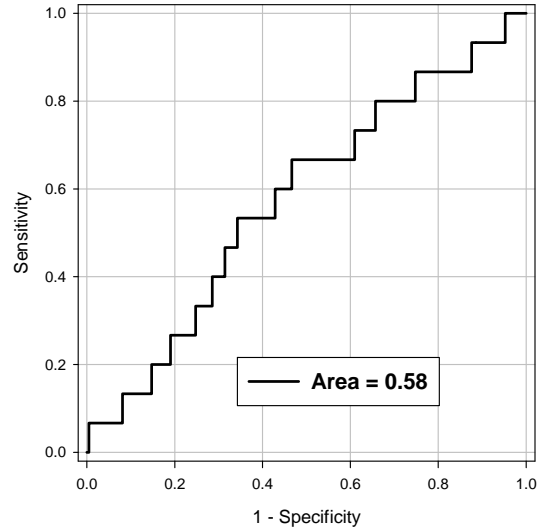
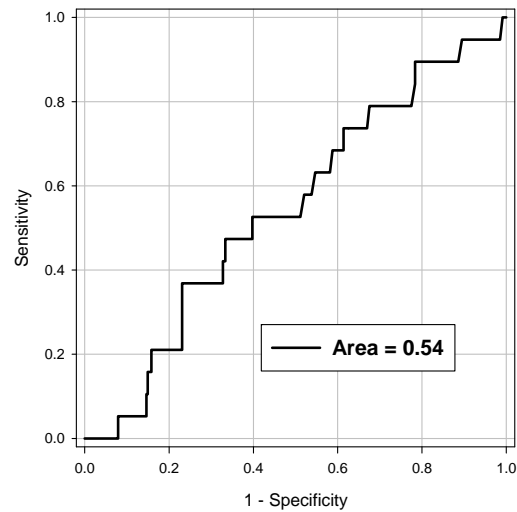Fig 11. ROC Curve evaluating the PCA analytical models for the ns IR regime in an air atmosphere.



Fig 13. ROC Curve evaluating the PCA analytical model for the fs IR regime in an air atmosphere.

The highest ROC curve area was found to be that of the ns IR regime, with an area of 0.58. This result leads to the conclusion that improvements to the model and the data acquisition have to be carried out to be able to conclude that the discrimination between organics can be performed in a single laser shot. In order to observe how the air atmosphere plays a role in the emission, spectroscopic signatures of the Fluoranthene organic residue are observed.
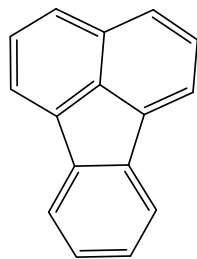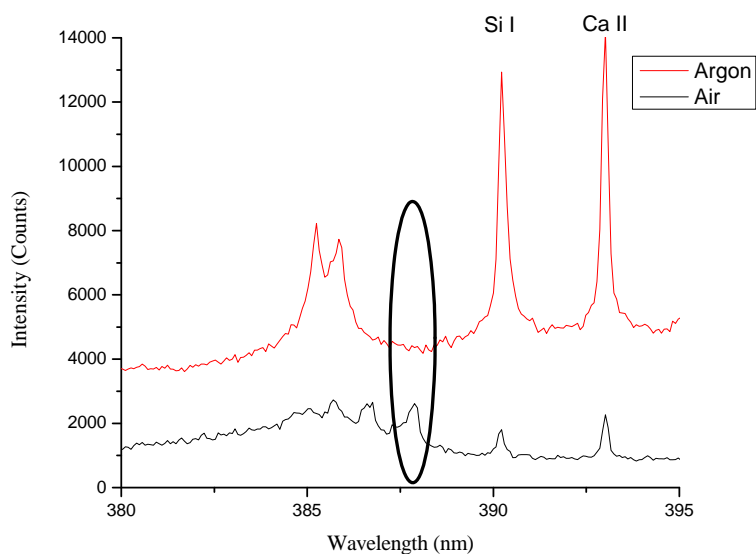
Fig 14. Fluoranthene Molecule



Fig 15. Comparison of spectra under air and argon in the nanosecond regime.

Figure 15 shows spectra centered in the CN violet bands ($\Delta v = 0$) at 388.5 nm and it is evident that there is molecular recombination occurring. This means that although there is a higher discrimination in the air, there is also a skewing of the data due to bias of the molecular recombination. Since CN recombination in the argon atmosphere is not evident, the analytical model that is constructed for air buffer gas is not based on information from the sample itself.

The femtosecond regime is found to have a slightly lower ROC curve area of 0.54. However, there is little evidence of molecular CN recombination, as shown in the spectra in Figure 16.
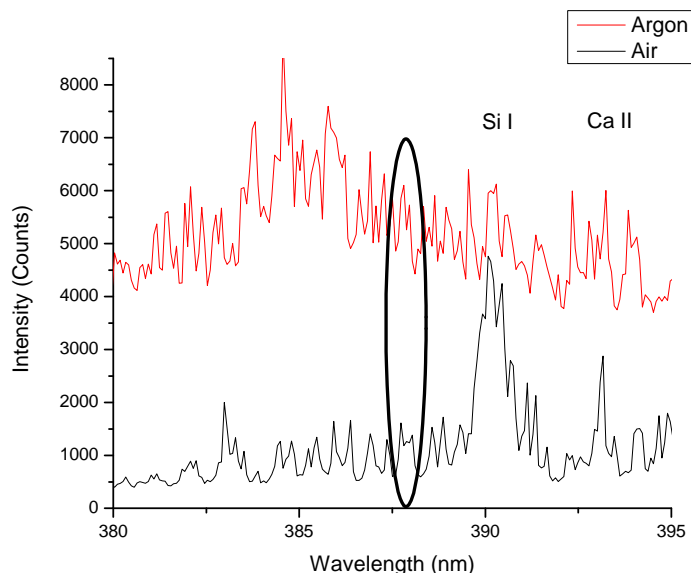
Fig 16. Comparison of spectra under air and argon in the femtosecond regime.

Any signal CN recombination emission is clearly contained within the signal-to-noise ratio in both the air and argon atmosphere. The evident lower signal-to-noise ratio in the femtosecond regime is also thought to contribute to the lower ROC curve area.

## 5.0 CONCLUSIONS

The analytical models as shown by ROC curves, make it clear that improvements need to be made to the data to which the models are applied. Improvements to factors such as the signal-to-noise ratio could improve the level of discrimination of organic residues on a non-metallic surface with a single laser shot. Caution has to be taken, however, in the nanosecond regime due to the bias towards molecular CN formation. Since there is no emission from molecular CN in argon atmosphere in the nanosecond regime, the model established in air is not solely based on sample information, because there are also contributions from the atmosphere. This is not the case in the femtosecond regime; however, the signal-to-noise ratio does not support single shot discrimination. Any CN formation from carbon and nitrogen recombination that may occur is not visible above the noise in either the air or argon atmosphere in the femtosecond regime. These results make a case for femtosecond laser interaction being a better candidate than nanosecond laser interaction to build a stable library for discrimination of organic compounds.

## ACKNOWLEDGEMENTS

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